Problem sheet 6

Please hand in your solutions before the lecture on Wednesday, 25th of November.

Problem 1 - Kinetic Theory

We can write the hamiltonian of N particles of a non-interacting ideal gas in a box of volume V as:

$$H = \frac{p^2}{2m} + U(q)\,, \tag{1}$$

with

$$U(q) = \begin{cases} 0 & \text{if the particle is inside the volume V} \\ \infty & \text{if the particle is outside of the volume V} \end{cases}$$

(a) Find the probability density of the velocity distribution. *(2 points)*

(b) Calculate the average velocity, the mean square velocity, the most probable velocity, and the average kinetic energy. *(4 points)*

Problem 2 - Gas with an internal structure

Consider a gas made up of N poli-atomic molecules, meaning, molecules with an internal structure. There is no interaction between the molecules, and given that the interaction potentials that correspond to the internal degrees of freedom depend only on the relative positions, the relative momenta, and the spins of the nuclei and the electrons, the motion of the centre of mass can be split off, this way we can write the Hamiltonian as

$$H_N = \sum_i \left(\frac{P_i}{2M_i} + v(q_i) + h_i \right)\,, \tag{2}$$

where P_i is the momentum of the centre of mass of the ith-molecule, M_i is the mass of said molecule, $v(q_i)$ is the confinement potential that restricts the molecules to be inside a finite volume V, and h_i is the hamiltonian of the internal variables.

(a) Show that the canonical and grand canonical partition functions are given by:

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \xi^N(\beta) \qquad\qquad \Xi = \exp\left[e^{\beta\mu} \frac{V\xi(\beta)}{\lambda_T^3} \right]\,, \tag{3}$$

where $\xi(\beta)$ is a function that only depends on the temperature, and λ_T is the thermal wavelength (explain what is the physical meaning of λ_T and of μ) . *(2 points)*

(b) Find the equation of state; write the energy, and the entropy, and show that the internal structure only contributes additively to this quantities. Finally, give an expresion for the chemical potential. *(2 points)*

(c) Show, using the Born-Oppeheimer approximation, that the function $\xi(\beta)$ can be separated as a product of functions related to the electrons and the nuclei, and show that the specific heat will be a sum of terms direct related to these degrees of freedom. *(2 points)*

(d) For a classical noble gas, the internal energy levels ϵ_i are the different nuclear and electronic states. The first electronic excited state is typically several eV, and the separation between all the posibble nuclear states in the ground state ranges between 10^{-5} and 10^{-4} eV. Calculate the electronic and nuclear contribution to the partition function, energy, and entropy for temperatures between 4.2 and 1000K. *(1 point)*

Problem 3 - Fluctuations

(a) Enunciate the fluctuation disipation theorem. Show the particular case for the specific heat: C_V is related to the equilibrium fluctuations of the energy as:

$$C_V = \frac{1}{N k_B T^2} \left[\langle E^2 \rangle - \langle E \rangle^2 \right] . \tag{4}$$

(3 points)

(b) Using this relation, show that the relative size of the fluctuations in the energy around it's mean value is neglegible when $\langle N \rangle \to \infty$. *(2 points)*

(c) Under which conditions can the size of this relative fluctutations be appreciable even in the thermodinamic limit? *(2 points)*

(d) What's the probability of an open system (one that can exchange energy and matter with the enviroment) having N particles? *(2 points)*

(e) Show that the mean quadratic deviation of the particle number can be written as:

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \frac{\langle N \rangle^2}{V} \kappa_T . \tag{5}$$

What can we say about the size of the fluctuations in the thermodinamic limit? And what about the equivalence between ensembles? *(2 points)*

Problem 4 - Ensembles

Let's start from the gibbs entropy for a probability distribution $p(n)$,

$$S = -k_B \sum_n p(n) \log(p(n)) . \tag{6}$$

(a) Using lagrange multipliers show that at fixed *total* energy and *total* particle number, the entropy is maximised by the grand canonical ensemble. What is the interpretation of the lagrange multiplier in this case. *(2 points)*

(b) Compare your results to the previous calculations done for the canonical and microcanonical ensembles. Regarding the constraint, what can we say is the difference between the three ensembles? And what is the meaning of the multipliers in each case? *(4 points)*